

Proceedings of the American Academy of Arts and Sciences.

VOL. XXXIII. No. 1. — JULY, 1897.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

ON THE TEMPERATURE COEFFICIENT OF THE POTENTIAL OF THE CALOMEL ELECTRODE, WITH SEVERAL DIFFERENT SUPERNATANT ELECTROLYTES.

BY THEODORE WILLIAM RICHARDS.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.



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Presented May 12, 1897. Received May 18, 1897.

THE well known Gibbs-Helmholtz formula for the temperature coefficient of a galvanic cell has been often tested,* with results which have usually been confirmatory. In 1885, however, among a number of satisfactory experiments, Gockel obtained a series of results † which he was at a loss to explain. He measured the temperature coefficient of calomel electrodes containing various supernatant electrolytes by setting up cells of the general form $\text{Hg-HgCl-MCl}_n\text{-HgCl-Hg}$, and maintaining the two ends at different temperatures. His results were as follows, each of the solutions being of half normal strength.

GOCKEL'S RESULTS.

Cell.	Temperature Coefficient.
$\text{Hg-HgCl-ZnCl}_2\text{-HgCl-Hg}$	+0.000675
$\text{Hg-HgCl-CdCl}_2\text{-HgCl-Hg}$	+0.000680
$\text{Hg-HgCl-BaCl}_2\text{-HgCl-Hg}$	+0.000440
$\text{Hg-HgCl-SrCl}_2\text{-HgCl-Hg}$	+0.000287
$\text{Hg-HgCl-NaCl-HgCl-Hg}$	+0.000119

These variations are not easily explicable. It is manifest that the usual equation for the temperature coefficient of a galvanic cell involving univalent ions — $\frac{d\pi}{dT} = \frac{\pi}{T} - \frac{Q}{\epsilon_0 T^2}$, in which π represents the potential, T the absolute temperature, Q the total change of energy (the heat of the reaction),

* Czapski, Wied. Ann., Vol. XXI. p. 239 (1884); Jahn, Wied. Ann., Vol. XXIV. pp. 21, 491 (1886); Loven, Z. Phys. Chem., Vol. XX. p. 456; Bugarszky, Z. Anorg. Chem., Vol. XIV. p. 145; and others.

† Wied. Ann., Vol. XXIV. p. 618; table on p. 638.

and ϵ_0 the quantity of electricity — does not directly apply in its present form. This equation is intended to represent the temperature coefficient of a complete cell, while we are considering that of a single electrode. In the cell $\text{Hg-HgCl-KCl-HgCl-Hg}$ the quantity dQ , which is neglected in the evolution of the above formula, may be an important factor; it is manifest that, since the two ends are alike, this quantity must represent the only difference between the heats of reaction at the hot and cold ends.

We might nevertheless expect the change of electromotive force with the temperature of a single electrode to be in general affected by the same factors as that of a cell; in other words, to be independent of every affecting cause but the potential, the absolute temperature, and the relation of the change of total energy to the quantity of electricity. We should expect the nature of the kation in the surrounding solution to have no direct influence, and hence the very large discrepancies observed by Gockel remain without explanation. The matter seemed worth investigation, and two years ago the present work was begun.

In the first place, many crude experiments were made for the purpose of orientation. These determinations were little more than a repetition of Gockel's, with the addition of a few with more dilute solutions, and the substance of them is presented in the first table below. Each of the figures is the average of a number of experiments, which agreed reasonably well with one another. Some of these experiments were made by Mr. Harold Edwards, to whom I would here express my thanks.

SERIES I.

PRELIMINARY.

Temperature 20° - 55° .

	Half normal.	Twentieth normal.	Fiftieth normal.
Hydric chloride	0.00030		
Sodic chloride	0.00062	.0008	.0009
Potassic chloride	0.000620009
Zincic chloride	0.00066		
Baric chloride	0.00059		

These results differ materially from Gockel's, which remain incomprehensible, but the irregularities are still sufficiently marked, especially in

the case of the hydrochloric acid, to warrant further investigation. But the exigencies of a research of this sort, the necessity of a large number of pure materials, and the long duration of each experiment, postponed the completion of the work for a much longer time than had been anticipated.

First, a word about the materials employed in the work which follows. The mercury was carefully purified chemically, and was also distilled in a vacuum. Four grades of mercurous chloride were used; in the first crude experiments "pure" calomel of commerce sufficed; subsequently a new portion of the salt was precipitated from an exceedingly dilute solution of mercurous nitrate, which was free from every impurity except mercuric nitrate, by the addition of hydrochloric acid; the third sample was made in this same way from very carefully prepared mercurous nitrate which had long been digested with mercury; and this third sample upon being twice successively sublimed yielded the fourth. When sufficiently washed with successive portions of a decinormal solution of potassic chloride, each of these preparations yielded "decinormal electrodes" of precisely the same potential, showing that as far as this work was concerned they were all alike. For most of the work the third sample, as being at the same time convenient and trustworthy, was adopted.

In order to free the hydrochloric acid which was used from possible traces of bromine and iodine, it was somewhat diluted and twice treated with a few crystals of potassic permanganate, each time boiling until all the chlorine was expelled. The acid was then twice successively distilled in a retort provided with a platinum condenser, rejecting the first and last portions of the distillate.

The soluble chlorides were also of a high grade of purity. Many had been prepared in the course of recent atomic weight determinations in this laboratory, and were far purer than is required in an investigation of the present sort, while others were prepared for this research. Especial pains were taken to exclude all anions except chlorine. The solutions were always made in such a way as to be as neutral as possible; they were in the first place prepared of the desired strength, and this strength was subsequently verified by a determination of the chlorine according to a modification of Volhard's method proposed independently by Sanger* and myself.† Although parallel experiments with boiled and unboiled solutions showed no difference in the temperature coefficient, the solutions were usually boiled for a short time in Jena glass vessels to expel most of the air. It soon appeared that the most serious cause of irregularity con-

* These Proceedings, XXVI. 34.

† These Proceedings, XXIX. 67.

sisted in accidental traces of water adhering to glass or mercury, which had the effect of unequally diluting the electrolyte in the cell, and thus causing concentration currents. If the apparatus is dried and the mercurous chloride is carefully washed with the appropriate solution before being added, the ease with which one may obtain consistent results is quite remarkable. The water used in these experiments, except in the first crude ones, was ordinary distilled water which had been redistilled from alkaline permanganate in a platinum still.

The first systematic experiments had for their aim the determination of the probable magnitude of the errors of observation due to accidental causes.

The apparatus consisted of two test tubes mounted in a convenient rack, in such a way that the liquid contents could be connected by a syphon. This tube could be filled by suction through a third arm above. Each test tube contained a few cubic centimeters of mercury, and above this mercury was placed a layer of finely divided mercurous chloride, surrounded by the electrolyte which filled the rest of the apparatus. If the layer was left undisturbed, its thickness was found to be unessential.

The two test tubes were kept at different temperatures by means of suitable baths of constant temperature, a steam jacket being employed for 100° , and pure cracked ice for 0° . At first the readings of the external thermometers were verified by means of very small accurate Anschütz thermometers placed in the test tubes themselves; but after many such verifications, which always resulted satisfactorily, this practice was discontinued, and the readings of the external thermometers alone were taken.

The differences of potential between the two layers of mercury were measured by the well known Ostwald-Poggendorff method,* within perhaps 0.0002 volt. The final reading was not taken until the temperature conditions had thoroughly adjusted themselves, an operation requiring from half an hour to many hours, according to circumstances.

In the first place a series of determinations of the effect of dilution upon the temperature coefficient of the electrode containing supernatant hydrochloric acid was made. The stronger solutions gave very uncertain results, and hence cannot be considered accurately determined; and correspondingly, in these the calomel was partially decomposed with separation of finely divided mercury. The reasons for these irregularities were better understood later.

* Hand- und Hilfsbuch phys. chem. Mess., pp. 251-255.

SERIES II.

THE EFFECT OF DILUTION.

$\text{Hg} - \text{HgCl} - (\text{HCl of varying strength}) - \text{HgCl} - \text{Hg}.$

Strength of Solution.	Temperature Coefficient between 20°-100°.
Twice normal	+0.000150 (?)
Normal	+0.000210 (?)
Half normal	+0.000250 (?)
Fifth normal	+0.000285
Tenth normal	+0.000324
Twenty-fifth normal	+0.000394
Fiftieth normal	+0.000438

It is evident that the temperature coefficient increases rapidly with dilution, as had already appeared from Series I. It is important, therefore, to adjust carefully the strength of the solutions to be used.

The effect of impurities and of mixing solutions was the next point to be tested. This effect could naturally be observed most satisfactorily by measuring cells containing mixtures of two electrolytes giving widely different temperature coefficients when pure; hence the third series of results, for which potassic and hydric chlorides were used.

SERIES III.

THE EFFECT OF MIXED SOLUTIONS (HALF NORMAL).

$\text{Hg} - \text{HgCl} - (\text{KCl} + \text{HCl}) - \text{HgCl} - \text{Hg}.$

Per Cent of Potassic Chloride Solution.	Per Cent of Hydrochloric Acid Solution.	Temperature Coefficient between 20° and 100°.
100	0	.00059
90	10	.00053
82	18	.00048
75	25	.00043 (?)
50	50	.00035
25	75	.00030
0	100	.00025

From these figures it is evident that small amounts of impurities can cause but slight differences in the result. The curve of changing temperature coefficient is a regular and gradual one.

The next series of results had for its object the determination of the effect of changing temperature. Heat evidently assisted the decomposition of mercurous chloride, for the precipitate in the warmer tube had always appeared the grayer of the two. Upon cooling to the same temperature, however, the potential always came back to zero, unless evaporation had been allowed to make one solution more concentrated than the other. Experiments in which the potential did not return to zero were rejected.

SERIES IV.

CHANGE OF TEMPERATURE COEFFICIENT WITH CHANGE OF TEMPERATURE.

Range of Temperature.	Temperature Coefficient. Hydrochloric Acid $\frac{1}{2}$ %.	Temperature Coefficient. Potassic Chloride $\frac{1}{2}$ %.
	Hg — HgCl — HCl — HgCl — Hg.	Hg — HgCl — KCl — HgCl — Hg.
0° — 25°	.00037	.00067
25° — 50°	.00026	.00063
50° — 75°	.00023	.00058
75° — 100°	.00021	.00056

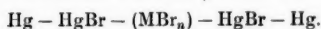
In the course of these experiments it had been noticed that an electrode upon shaking always yielded a higher potential than after it had remained standing. This was especially the case with concentrated solutions and high temperatures. This fact has been observed by Coggeshall,* who recommends a layer of sand or small pebbles as a means of preventing the agitation. The irregularity in question appeared to show a lack of homogeneity in the solution, and it seemed important to explain the matter before proceeding further.

With this end in view, several experiments were made with bromides instead of chlorides. Here the irregularity was found to be vastly greater, and the precipitated bromide became gray at once even in cold solutions. Normal solutions gave results which varied over the wide limits given below, and even these cannot be considered the possible limits. Decinormal solutions were much less uncertain, but these seemed to be as much affected as normal solutions of chlorides.

* Z. Phys. Chem., XVII. 62.

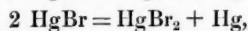
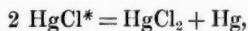
SERIES V.

BROMIDES BETWEEN 0° AND 30°.



Electrolyte = MBr _n .	Normal Solution.	Decinormal Solution.
Hydrobromic acid00044 to .00047	
Strontic bromide00061 to .00068	.00079
Zincic bromide00065 to .00077	.00090

It was at once evident that the cause of the difficulty was the occurrence of the following reactions:—



which seem to be effected by a "catalytic" action of the haloid ions in the solution.

This reaction has already been observed by Miahle,[†] but a confirmation seemed desirable. Numerous solutions decanted from the present experiments were filtered, and found by testing with stannous chloride or hydrogen sulphide to contain mercuric salts, — the normal bromides very large amounts, the normal chlorides and decinormal bromides much less, and the decinormal chlorides very little. In order to subject the method to a rigid test, a quantity of mercurous chloride was prepared with very great precautions, being made and kept wholly in non-actinic light or darkness. This material after very thorough washing was divided between a number of bottles, to each of which was added a carefully made standard solution of some chloride. Three bottles of normal potassic chloride were made in this way, one being carefully boiled, wholly filled, while hot, hermetically stoppered, and kept in perfect darkness, another being half filled and left in contact with air, but also in darkness, and the third, otherwise like the second, being exposed to bright sunlight. Bottles similarly filled with (4) decinormal potassic chloride, (5) normal zincic chloride, and (6) normal hydrochloric acid, were also

* The adoption of HgCl instead of Hg₂Cl₂ as the formula of mercurous chloride is purely for convenience. The true formula of this substance in the solid state seems to me doubtful.

† J. Pharm., XXVI. 108; Ann. Chim. et Phys., (3.), V. 177.

prepared in yellow light, and all excepting the third were allowed to stand nearly three weeks in total darkness with occasional shaking before being filtered. Upon the expiration of this time thirty cubic centimeters of each of the filtrates were heated and treated with an excess of a solution of hydric sulphide, the zincic solution being acidified with hydrochloric acid. The precipitates were allowed to settle upon the bottoms of test tubes, where a very fair guess as to their relative quantities could be obtained. The three normal potassic chloride solutions and the hydrochloric acid appeared to yield equal amounts of mercuric sulphide, the zincic chloride very slightly less, while the decinormal solution of potassic chloride deposited no precipitate, and showed only the faintest possible coloration. These experiments showed that:—

- (a) The reaction $\text{Hg}_2\text{Cl}_2 = \text{HgCl}_2 + \text{Hg}$ is an undoubted fact.
- (b) Light has no considerable effect on this reaction.
- (c) Dissolved air is also not the essential factor.
- (d) Different chlorides produce effects not very different.
- (e) The concentration of the chlorine ions in solution is a most important factor.
- (f) About a decigram of mercuric chloride is formed in a litre of a normal solution of potassic chloride at 20° .

The equilibrium is an interesting one; it will receive further attention in this laboratory.

That this mercuric salt actually increases the potential of the electrode containing it was easily proved by adding mercuric chloride to a decinormal calomel electrode, and comparing this electrode with a similar one in which the alkaline chloride had the same concentration. Invariably the mercuric salt raised the potential of the electrode in question. After long standing this difference gradually lessened, as the mercuric chloride was reduced; but upon shaking the difference at once appeared again. Undoubtedly in time all the excess of mercuric chloride would be reduced, until the constant amount which seems to be in equilibrium with mercurous chloride and mercury under the given conditions was reached, when the difference would disappear at constant temperature. The chief conditions of experiment being now determined, the next step was to make an accurate series of determinations of the temperature coefficient of the potential of the cells $\text{Hg} - \text{HgCl} - \text{MCl}_n - \text{HgCl} - \text{Hg}$.

Since low temperatures had been found less likely to cause the disturbing formation of mercuric salt, the two temperatures 0° and 30° were selected as the most suitable for the present purpose. Since the degree of dilution had been found to produce such an important difference in

the conditions and result, solutions of three very different strengths were used. Obviously the solutions should be allowed to remain perfectly quiet at their respective temperatures for a time sufficient to allow complete establishment of the equilibrium. This time varied from several hours, in the case of the normal solution, to a few minutes, in the case of the most dilute solutions. Perhaps the best idea of the rapidity of the adjustment of equilibrium with dilute solutions may be obtained from the following series of observations, which is a fair sample. A tenth normal solution of baric chloride was placed in the apparatus with mercury and mercurous chloride, and one arm was heated to 30° in a thermostat, while the other was packed in ice.

At the very beginning of the experiment,	potential = 0.0000 volt.
After five minutes,	" = 0.0200 "
After ten minutes,	" = 0.0218 "
After twenty minutes,	" = 0.0217 "
After a hundred minutes,	" = 0.0218 "

The whole apparatus was now placed in a thermostat at 30° , and a new series of observations was made.

At the beginning of the experiment,	potential = 0.0218 volt.
After one minute,	" = 0.0050 "
After two minutes,	" = 0.0020 "
After three minutes,	" = 0.0008 "
After four minutes,	" = 0.0001 "
After five minutes,	" = 0.0000 "
After ten minutes,	" = 0.0000 "
After sixty minutes,	" = 0.0000 "

Centinormal solutions behaved in the same praiseworthy fashion, but normal solutions were much more unsteady, and required a very much longer time.

As was to have been expected, decinormal and centinormal solutions gave a constant potential even when agitated, for no essential amount of mercuric salt is formed in these cases.

In order to get rid of the thermo-electric error of having the two junctions of platinum and mercury at different temperatures, an apparatus was made which allowed them to be kept at the same temperature. The mercury in each arm was connected by means of a capillary tube filled with mercury to a suitable cup in the thermostat at 30° , where the two wires from the electrometer were each connected. The tube for the

electrolyte was wide in order to allow of measurement through the small conductivity of the dilute solutions. The accompanying sketch will give a better idea of the arrangement. The Peltier effect above mentioned was neglected by Gockel, because it usually amounted to less than one per cent of the whole potential to be measured; but in the present series I thought the safer course was to eliminate it.

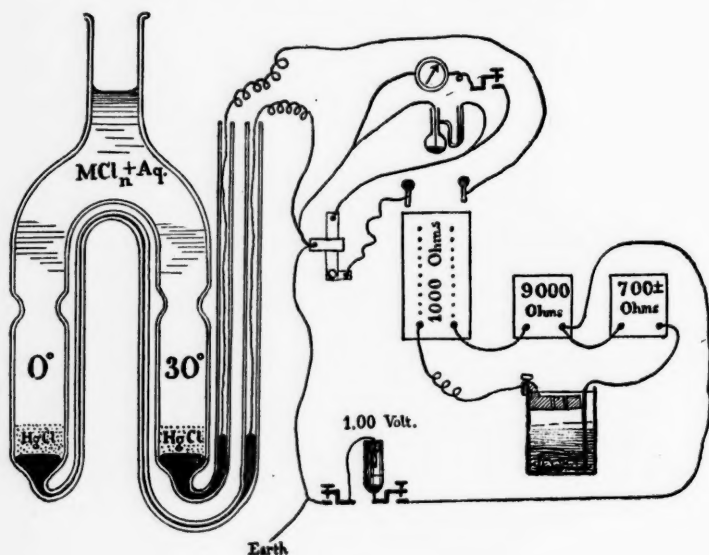


DIAGRAM OF APPARATUS.

The glass part at the left of the diagram is drawn about one third of the actual size. The remainder of the apparatus is not drawn to scale, being annexed merely to show the connections. For those familiar with the Ostwald-Poggendorff method no explanation is necessary.*

The potentials were measured as before by the Poggendorff compensation method, a sensitive galvanometer as well as a very sensitive Lippmann electrometer being used for the normal and decinormal solution, and the electrometer alone for the centinormal. In order to secure greater accuracy, the Ostwald potential box* of 1,000 ohms was connected with a Daniell "gravity" cell, and $9,700 \pm$ ohms external resistance, so that

* Hand- und Hilfsbuch phys. chem. Mess., pp. 252, 253.

the extremities of the box gave a difference of potential of just 0.1000 volt. This potential was verified and adjusted from day to day by means of a suitably connected Helmholtz one-volt cell, which in its turn had been compared with several standard Clark and Weston cells. The "gravity" cell remained admirably constant in potential.

The measurements involving decinormal solutions are the most accurate of those given below. The resistance of the centinormal solutions tended to diminish the accuracy with this dilution, because the galvanometer became ineffective; while the formation of mercuric chloride made uncertain the very easily measured potential of the normal solution. Many of the figures, especially those referring to normal hydric, sodic, and potassic chlorides, represent determinations made from a number of solutions of substances prepared in different ways; since these always gave the same result, only one figure is given for each.

SERIES VI.

CHLORIDES BETWEEN 0° AND 30°.

Including a larger number of Electrolytes. Cell = $\text{Hg} - \text{HgCl} - \text{MCl}_n - \text{HgCl} - \text{Hg}$.

MCl_n .	Temperature Coefficient. Normal Solution.	Temperature Coefficient. Decinormal Solution.	Temperature Coefficient. Centinormal Solution.
Hydrochloric acid . . .	0.00033	0.00054	0.00066 (?)
Lithic chloride	0.00063	0.00083	0.00100
Sodic chloride	0.00056	0.00078	0.00095
Potassic chloride . . .	0.00061*	0.00079	0.00094
Calcic chloride	0.00053	0.00076	. . .
Strontic chloride . . .	0.00053	0.00074	0.00092
Baric chloride	0.00053	0.00073	0.00092
Magnesian chloride	0.00076	0.00096
Zincic chloride	0.00063	0.00078	0.00095
Cadmic chloride	0.00069	0.00082	0.00097
Ammonic chloride . . .	0.00058 (?)	0.00085 (?)	0.00102 (?)

* This result is somewhat lower than that obtained by Coggeshall and others, but since I repeatedly obtained it, I cannot but believe that other results must have been complicated by some modifying circumstance. See Z. Phys. Chem., XVII. 85.

Hydrochloric acid evidently occupies a position quite anomalous, and ammoniac chloride also, at the other extreme, produces an electrode with a temperature coefficient considerably different from the average of the other metals. The presence of hydrogen ions in the one case, and the tendency toward the formation of amido compounds in the other might well tend to separate these two cases from the others, hence the consideration of these substances will be postponed. The remarks which immediately follow apply to the other chlorides.

It is interesting to note that each successive dilution produces about the same change in the temperature coefficient (on the average 0.00019 to 0.00018 volt). In other words, if we take the concentration of the centinormal solution as 1, of the decinormal solution as 10, and of the normal solution as 100, it is manifest that the changes in the temperature coefficient are proportional, not to the changes in the concentration itself, but to the changes in the logarithm of the concentration.

This relation immediately reminds one of the Nernst formula, in which the potential itself is a logarithmic function of the osmotic pressure of the ions; for this osmotic pressure is with dilute solutions nearly proportional to the concentration of the salt in the solution. With this idea in view, it becomes at once a matter of interest to correct the results given above for the concentrations of the respective ions; it is obvious that the normal solution of cadmic chloride must be much weaker in chlorine ions than a normal solution of potassic chloride. In order to attain this end one must first construct a logarithmic formula for the temperature coefficient involving the concentration of the surrounding electrolyte; and naturally the Nernst formula is the most convenient starting point for this construction. Considering the electrode in question in the simplest way as a source of negative ions, its potential may be assumed to have this value:—

$$\pi = \frac{RT}{\epsilon_0} \ln \frac{P}{p},$$

in which π = the potential difference in question, R = the gas-constant $= 1.96 \times 4.24$ volt-coulombs, $\epsilon_0 = 96,540$ coulombs, \ln indicates a natural logarithm, P is the "outward tendency" (solution tension) of the chlorine in the electrode, p is the osmotic pressure of the chlorine ions in the surrounding solution, and T is the absolute temperature.

The differential of this equation is

$$d\pi = \frac{R}{\epsilon_0} \left[dT \ln \frac{P}{p} + T \left(\frac{dP}{P} - \frac{dp}{p} \right) \right];$$

for we cannot assume either P or p to be constants with this form of electrode. Dividing by $d T$, we obtain an expression for the temperature coefficient of a single electrode, as follows:—

$$\frac{d\pi}{dT} = \frac{R}{\epsilon_0} \ln \frac{P}{p} + \frac{RT}{\epsilon_0} \left(\frac{dP}{PdT} - \frac{dp}{pdT} \right).$$

Since the general tendency of the actual results is logarithmic, my observations show that the last quantity must be so small as to be without any very great influence.

In order to compute the maximum influence of this last quantity, let us assume that P is constant, hence that $dP = 0$; and the quantity considered becomes

$$-\frac{R}{\epsilon_0} \times \frac{T}{dT} \times \frac{dp}{p}.$$

But according to the law of Dalton, which applies approximately to ions,

$$T : dT = p : dp, \text{ or } \frac{T}{dT} \times \frac{dp}{p} = 1.$$

Hence in this case the last term becomes $-\frac{R}{\epsilon_0} = -0.000086$, which is only about a tenth of $\frac{d\pi}{dT}$ itself.

For the present, then, let us neglect this last factor, assuming that on the average $\frac{dP}{P} = \frac{dp}{p}$, and our formula becomes

$$\frac{d\pi}{dT} = \frac{R}{\epsilon_0} \ln \frac{P}{p} = 0.000198 \log \frac{P}{p},$$

in which log stands for the common Briggs's logarithm.

In this case, since we are considering a negative ion, and $P > p$, it is obvious that the potential of the mercury with respect to the solution must increase with the temperature, an inference which corresponds with the facts. The current may be supposed to be carried by chlorine ions moving from the hot electrode, where they are given off, to the cold, where they combine with mercury.

We have now at our disposal a formula of the sort required; the table above furnishes values for $\frac{d\pi}{dT}$, and p may easily be calculated from the relation $\alpha = \text{the dissociation factor} = \frac{\lambda_v}{\lambda_\infty}$, which changes only

very slightly with the temperature. Hence we may calculate the value of P from one case, and see if the same value applies in others. If for convenience we take as our unit for p the pressure exerted by a gram equivalent of the anion when dissolved in a litre of water, it is obvious that for normal solutions $p = a$, for decinormal solutions $p = \frac{a'}{10}$, and for centinormal solutions $p = \frac{a''}{100}$. Thus with a centinormal solution of potassic chloride, where ninety-four* per cent of the salt is dissociated, we have

$$\begin{aligned}\log P &= \frac{d\pi}{dT} \frac{1}{0.000198} + \log \frac{a''}{100} \\ &= \frac{.00094}{.000198} + \log \frac{0.94}{100} = 4.747 - 3 + 0.973 = 2.720.\end{aligned}$$

Hence $P = 525$. In a similar way we may find for sodium $P = 585$; evidently 550 represents a fair average value which we may adopt for this quantity upon the scale of measurement used for p . The centinormal solutions were chosen in this case because here the disturbing reaction $\text{Hg}_2\text{Cl}_2 = \text{HgCl}_2 + \text{Hg}$ is the least active. In order to get an idea of the probable error of our many hypotheses, it is well to calculate backwards and obtain a theoretical value for the temperature coefficient for other centinormal solutions besides potassic chloride from the equation

$$\frac{d\pi}{dT} = 0.000198 \log \frac{550 \times 100}{a''},$$

in which the above named values of P and p have been substituted. Performing these substitutions, and, taking for the values of the electrical conductivities the data obtained by Kohlrausch at 18° , we obtain the following table.

* This value for a'' is of course only approximate; but the approximation is sufficiently accurate, for a large difference in a makes only a very small difference in the temperature coefficient.

COMPARISON OF THEORETICAL AND ACTUAL TEMPERATURE COEFFICIENTS.

CENTINORMAL SOLUTIONS.

Electrolyte.	$\alpha = \frac{\lambda_p}{\lambda_\infty}$	Temperature Coefficient of the Potential.		Difference.
		Calculated.	Found.	
Lithic chloride . .	0.92	0.00095	0.00100	+ 0.00005
Sodic chloride . .	0.93	0.00095	0.00095	+ 0.00000
Potassic chloride .	0.94	0.00095	0.00094	— 0.00001
Calcic chloride . .	Data insufficient.	0.00095 ?	0.00092 ?	. . .
Strontic chloride .	Data insufficient.	0.00095 ?	0.00092	. . .
Baric chloride . .	0.88	0.00095	0.00092	— 0.00003
Magnestic chloride .	0.885	0.00095	0.00096	+ 0.00001
Zincic chloride . .	0.885	0.00095	0.00095	± 0.00000
Cadmic chloride .	0.75	0.00097	0.00097	± 0.00000
Average				0

The examination of this table shows that the slight differences in the degree of dissociation of the various chlorides should produce no essential difference in the temperature coefficients, except in the case of cadmium, where the theoretical value corresponds exactly with that actually found. The theoretical values for cadmium, zinc, and magnesium agree sufficiently well with the experimental values, but those for barium, strontium, and calcium are too high, while that for lithium is too low. The potassium and sodium are of course the standards.

It becomes now a matter of great interest to apply this formula to the more concentrated solutions, using the value of $P = 550$, which has thus been computed from the relations of centinormal potassic and sodic chlorides. Such an application furnishes us with the best possible test of the legitimacy of our hypotheses. In the same terms as before the formula for decinormal solutions becomes

$$\frac{d\pi}{dT} = 0.000198 \frac{550 \times 10}{a'},$$

and that for normal solutions becomes

$$\frac{d\pi}{dT} = 0.000198 \frac{550}{a}.$$

Since calcium and strontium are essentially like barium, and magnesium is very similar to zinc, the following six metals may be taken as fair samples of the behavior of various chlorides.

COMPARISON OF THEORETICAL WITH THE ACTUAL TEMPERATURE COEFFICIENTS.

BARIUM CHLORIDE.				
Strength of Solution.	$\alpha = \frac{\lambda_p}{\lambda_\infty}$	Temperature Coefficients of Potential.		Difference.
		Calculated.	Found.	
Normal	0.57	0.00059	0.00053	— .00006
Decinormal . .	0.75	0.00077	0.00073	— .00004
Centinormal . .	0.88	0.00095	0.00092	— .00003
Average				— .00004
CADMIUM CHLORIDE.				
Normal	0.20 ±	.00068	.00068	± .00000
Decinormal . .	0.47 ±	.00081	.00082	+ .00001
Centinormal . .	0.75 ±	.00097	.00097	± .00000
Average				0
SODIUM CHLORIDE.				
Normal	0.67	0.00058	.00056	— .00002
Decinormal . .	0.84	0.00076	.00078	+ .00002
Centinormal . .	0.93	0.00095	.00095	± .00000
Average				+ 0.00000

ZINCIC CHLORIDE.				
Strength of Solution.	$\alpha = \frac{\lambda_{\beta}}{\lambda_{\alpha}}$	Temperature Coefficients of Potential.		Difference.
		Calculated.	Found.	
Normal	0.50	0.00060	0.00063	+ .00003
Decinormal . .	0.74	0.00077	0.00078	+ .00001
Centinormal . .	0.88	0.00095	0.00095	\pm .00000
Average				+ .00001
POTASSIC CHLORIDE.				
Normal	0.75	0.00057	+ .00061	+ .00004
Decinormal . .	0.86	0.00075	+ .00079	+ .00004
Centinormal . .	0.94	0.00095	+ .00094	- .00001
Average				+ .00002
LITHIC CHLORIDE.				
Normal	0.62	0.00058	+ .00063	+ .00005
Decinormal . .	0.81	0.00076	+ .00083	+ .00007
Centinormal . .	0.92	0.00095	+ .00100	+ .00005
Average				+ .00006

It is evident that there is a general tendency towards the fulfilment of the conditions required by the formula. The agreement in the case of cadmium, where the effect of irregular dissociation is most apparent, is quite remarkable. The agreement in the cases of sodium and zinc is not bad; but the deviations in the case of barium on the one hand and that of potassium and lithium on the other are quite too large to be accounted for upon the basis of experimental error. It is obvious that in these cases we have some modifying circumstances; our assumption that $\frac{dP}{P} = \frac{dp}{p}$ is evidently not justified. The attempt to penetrate further into the

matter by the analysis of the probable causes of P reveals that this quantity may be dependent upon several ultimate factors, — such as the changing solution pressure of the chlorine ions due to changes in temperature and the already detected formation of mercuric chloride, the changing solubility of mercurous chloride with the temperature and the presence of other chlorine ions, as well as the possibly varying “heat of formation” of mercurous chloride. Moreover, a modifying circumstance, entirely disconnected with the electrode itself, lies in the possible generation of potential from the contact of the warm solution with the cold solution. That these influences are subordinate ones, except in the cases of hydrochloric acid and ammonia, is indicated by the above tables; but further explanation must carry one too far into the region of hypothesis, and had better be postponed until a more satisfactory experimental basis is established.

The results of this paper may be summed up as follows: —

(a) The temperature coefficient of the potential of the calomel electrode increases with the dilution of the electrolyte.

(b) The kation of the electrolyte influences the result by affecting the degree of dissociation of the chloride in solution.

(c) Both of these effects may be approximately computed by a simple logarithmic formula based upon Nernst's hypothesis.

(d) The accuracy of the results is, however, affected by at least one important modifying influence, the “catalytic” decomposition of mercurous chloride into mercuric chloride and mercury.

(e) This side reaction is responsible for the slight inconstancy of the normal calomel electrode.

(f) The “decinormal electrode” is much more uniform in its behavior than the normal, and hence for some purposes might be a more useful means of measuring potential differences.

(g) Hydrochloric acid and ammoniac chloride are anomalous in their behavior.

This research was begun in the Laboratory of Physical Chemistry at Leipsic, upon the suggestion of Professor Ostwald. It was continued by his kind consent at the Chemical Laboratory of Harvard College, and I hope that some of the problems left unsettled may be solved by future work here. Especially is it my intention to apply the differential equations to other cases, such as an electrode of zinc in a zinc salt.

CAMBRIDGE, MASS., May, 1897.